The Crystal and Molecular Structure of an Asymmetric Diacetylene Monomer, 1-(4'-dimethylaminobenzoyloxy) -6-(3", 5"-dinitrobenzoyloxy)-2, 4-hexadiyne

by

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Summary

The crystal and molecular structure of an asymmetric diacetylene derivative monomer has been determined from x-ray diffraction data. The crystals are monoclinic, $P2_1/c$ with $Z = 4$ in a unit cell having dimensions, $a = 11.116(1)$ Å, $b = 13.429(2)$ Å, $c = 14.672(3)$ Å, $\beta = 106.84(6)°$. The structure was solved by direct methods and refined by least-squares techniques to an R_F of 6.2% for 1991 reflections. The diacetylene backbone chains are almost perfectly parallel to the ac-plane; however, they are displaced from each other in the [010] direction. The solid state polymerization mechanism is discussed with respect to the geometric disposition of the diacetylene chains, which in this crystal are too far apart to permit polymerization by means of 1, 4-addition, consistent with the Baughman mechanistic model.

Introduction

The search for macroscopic single crystals of polymers, which are useful in the study of solid-state properties and the investigation of possible applications to technological needs, has been conducted for a number of years. These efforts have been unsuccessful, except for the topochemical polymerization of certain conjugated compounds[1]. Several classes of organic compounds can undergo polymerization when exposed to high-energy radiation[2,3,4,5,6]. Such reactions provide a means of direct synthesis of highly crystalline polymers and macromolecular systems. A direct correlation has been established between the geometry and stereochemistry of the molecules in the monomer crystal and the crystalline molecular structure of the polymer[7,8,9,10,11,12].

One of these reactions is the topochemical polymerization of monomer diacetylenes with conjugated triple bonds. This reaction is known to proceed as a 1,4-addition to the conjugated triple bonds according to:

$$n(R-C\equiv C-C\equiv C-R') \longrightarrow (\overset{R}{\underset{R'}{\diagdown}} C-C\equiv C-C \diagup)_n$$
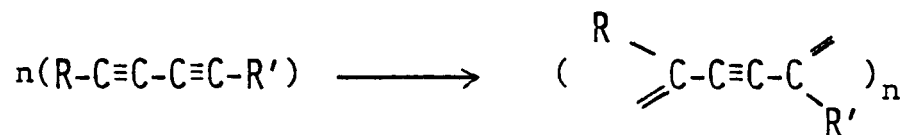
where R and R' are various substituents. Single crystals of a number of these monomers and polymers have been studied by x-ray and neutron diffraction and Raman-spectroscopy, and their stereochemistry has been established[7,13,14,15,16,17,18,19].

Stereochemical criteria governing the disposition of the molecules in the monomer crystal required in order to bring about polymerization were advanced by Baughman[9] based on crystallographic studies and the principle of least motion. In such a model, the polymerization reaction is described as a rotational motion of the structural units with a specific spacing of the reactive diacetylene chains along the growth direction (some lattice vector $\vec{a}$) having a period d_1 and making an angle γ_1 with vector $\vec{a}$ (see Fig. 1). According to this theory, the ideal parameters d_2 and γ_2, in the polymer form, have values of 5.0 Å and 13.0°. The reactivity of a monomer crystal would depend, therefore, on how close d_1 and γ_1 are to d_2 and γ_2. However, a number of other factors influence reactivity and it is not possible to make quantitative predictions about specific compounds.

Since we were able to obtain good quality single crystals of the title substituted diacetylene compound ($R = -CH_2OCO-C_6H_5-N(CH_3)_2$, $R = -CH_2OCO-C_6H_5-(NO_2)_2$) we considered it of interest to carry out an x-ray diffraction analysis, in hopes that the results would provide more insight into the relationship between structure and reactivity of these very interesting and promising diacetylene derivative materials.

Experimental Part

Large red transparent crystals of the title compound were obtained by crystallization from a CH_2Cl_2/hexane mixture. These crystals are stable in light and air, and showed no decomposition under x-ray radiation during the length of the experiment. A small triangular shaped slab (0.2 x 0.2 x 0.06 mm) was used for the data collection. The unit cell parameters were obtained from 15 high-angle reflections refined on the diffractometer. These are: $a = 11.116(1)$ Å, $b = 13.429(2)$ Å, $c = 14.672(3)$ Å, $\beta = 106.84(6)°$, $Z = 4$, $d_{calc.} = 1.433$ g/cm^3, $P2_1/c$. The intensities were measured with a single-crystal diffractometer (E-N CAD4) using $\theta/2\theta$ scans and $CuK\bar{\alpha}$ ($\lambda = 1.5418$ Å) graphite-monochromated radiation. A total of 5590 ($\theta_{max} = 60$ °) doubly-equivalent reflections were collected which were averaged and selected ($I > 3\sigma(I)$) to give 1991 independent reflections for the analysis. No absorption correction was applied.

The structure was solved by direct methods using MULTAN[20]. Refinement by full-matrix least-squares with anisotropic thermal parameters led to a final R-factor (on F) of 6.2% and a G.O.F. = 1.498[21]. The hydrogen atom positions were refined with fixed isotropic thermal factors. A final Fourier difference map showed no electron density peaks greater than 0.47 e$^-$/Å^3. The final positional and thermal parameters are given in Tabs. 1 and 2*.

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*A list of structure factors may be obtained from M.V.

Results and Discussion

A projection of the structure on the ac-plane is drawn in Fig. 2. This diagram shows the diacetylene backbone chains parallel to each other, but situated at different levels along the b-axis. The four atoms (C2 to C5) comprising the diacetylene backbone lie nearly in the ac-plane, with a maximum deviation of 0.090 Å and a mean deviation of 0.046 Å. Even the extended chain (C1 to C6) is quite parallel to this plane (maximum deviation 0.396 Å and mean deviation 0.111 Å). This planarity is common to many diacetylene derivatives, and only the side-chains are inclined with respect to the chain to accommodate crystal packing requirements[22,23]. The bond distances and bond angles of the diacetylene chain are given in Fig. 3. It can be seen that the triple bonds (C2-C3 and C4-C5) have their expected values compared to the average $\langle C \equiv C \rangle = 1.206(4)$ Å and to other diacetylenes[22,23]. The effect of these triple bonds on the adjoining "single" bonds is evident by their effective values of 1.460(6) Å and 1.478(6) Å for C1-C2 and C5-C6, and of 1.377(6) Å for C3-C4. Similar bond distance and angle values have been observed in 2,4-hexadiynediol and other substituted diacetylenes[23]. All other bond distances and bond angles in the molecule conform to the general accepted values for organic compounds (Tab. 3). The cohesive forces in the crystal are due to hydrogen bonding and other van der Waals interactions. The fact that all hydrogen atoms are bonded to carbon, any hydrogen bonding interaction would certainly be weak. Several C-H....O intermolecular interactions seem to be of importance:

O(2).....H(16) = 2.695(5) Å, O(6).....H(12) = 2.771(5) Å and

O(7).....H(6) = 2.673(5) Å.

The disposition of the molecules with respect to each other, and in particular that of the diacetylene backbone chains, determines the metric and angular relationships between these chains. The unit cell contains two different symmetry operators (2_1 and $\bar{1}$), leading to two different interchain distances and giving rise to two sets of Baughman geometric parameters (d and γ)[9]. These are:

d_1 = 7.314 Å γ_1 = 78.71° (molecules related by 2_1).

d_1' = 5.555 Å γ_1' = 42.83° (molecules related by $\bar{1}$).

The comparison of these values to the critical distance and angle (d_2 = 5.0 Å, γ_2 = 13.0 Å) determined by Baughman as ideal values for solid state polymerization indicates that the observed values are too large to allow polymerization to take place. This clearly explains why this particular asymmetric diacetylene is not reactive towards polymerization with any radiation sources - visible, UV, or x-ray. The disposition adopted by the molecules in the crystalline state, surely as a consequence of the steric and repulsive interactions of the R and R' groups which are rather bulky, results in interchain separations which are too long to allow the 1, 4-addition reaction to take place. We can conclude then, that the stability of the title compound to polymerization is consistent with the Baughman model: The size and functionability of the R and R' groups as well as the

rigidity of the local environment are critical in allowing a monomer to have optimal d_1 and γ_1 values (see Tab. 4). It can be further concluded that symmetric (R = R') diacetylenes are more likely to have these optimal values than asymmetric ones, and thus be more reactive.

Acknowledgments

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Figure Captions

Figure 1.   Disposition of the diacetylene chains in the monomer
and polymer crystal and the ideal geometric parameters
for solid state polymerization.

Figure 2.   Projection on the (101) plane of the cell content
showing the disposition of the chains.

Figure 3.   Backbone chain of the diacetylene monomer.   Distances
($\pm$ 0.006 Å) and angles ($\pm$ 0.5°).

Table 1. Positional and Thermal Parameters for $C_{22}H_{17}N_3O_8$.

Atom	x	y	z	Beq (Å^2)[a]
C(1)	0.7683(5)	0.4103(4)	0.7321(3)	5.0(2)
C(2)	0.6722(5)	0.4088(3)	0.7820(3)	4.2(2)
C(3)	0.5917(5)	0.4088(3)	0.8209(3)	4.0(2)
C(4)	0.4984(5)	0.4117(3)	0.8655(3)	3.1(2)
C(5)	0.4194(5)	0.4187(3)	0.9035(3)	3.1(2)
C(6)	0.3268(5)	0.4383(4)	0.9561(3)	3.2(2)
C(11)	0.7444(4)	0.5570(3)	0.5175(3)	2.7(2)
C(12)	0.6264(4)	0.6017(3)	0.5038(3)	2.7(2)
C(13)	0.5818(4)	0.6721(3)	0.4362(3)	2.9(2)
C(14)	0.6526(5)	0.7039(3)	0.3748(3)	2.9(2)
C(15)	0.7697(5)	0.6563(4)	0.3869(3)	3.5(2)
C(16)	0.8154(4)	0.5852(3)	0.4559(3)	2.9(2)
C(17)	0.7979(5)	0.4858(3)	0.5938(3)	2.9(2)
C(18)	0.4887(6)	0.8231(4)	0.2971(4)	4.3(2)
C(19)	0.6839(7)	0.8097(5)	0.2473(5)	5.1(2)
C(21)	0.0301(4)	0.3063(3)	0.9330(3)	3.3(2)
C(22)	0.0268(4)	0.2392(3)	0.8605(3)	2.6(2)
C(23)	-0.0711(4)	0.1710(3)	0.8352(3)	2.6(2)
C(24)	-0.1664(4)	0.1685(4)	0.8780(3)	2.9(2)
C(25)	-0.1581(4)	0.2377(3)	0.9503(3)	2.9(2)
C(26)	-0.0644(5)	0.3064(3)	0.9778(3)	3.2(2)
C(27)	0.1348(5)	0.3793(4)	0.9679(3)	3.0(2)
N(1)	0.6105(4)	0.7770(3)	0.3099(3)	3.9(2)
N(2)	-0.2610(4)	0.2368(3)	0.9956(3)	3.7(2)
N(3)	-0.0767(4)	0.0997(3)	0.7577(3)	3.5(2)
O(1)	0.7209(3)	0.4736(2)	0.6496(2)	3.3(1)
O(2)	0.8962(3)	0.4430(3)	0.6083(2)	4.0(1)
O(3)	0.2219(3)	0.3690(2)	0.9217(2)	2.9(1)
O(4)	0.1403(3)	0.4396(3)	1.0298(3)	4.8(1)
O(5)	-0.2484(4)	0.2930(3)	1.0651(3)	5.2(1)
O(6)	-0.3508(3)	0.1831(3)	0.9628(3)	4.8(1)
O(7)	-0.1657(4)	0.0417(3)	0.7353(3)	5.1(1)
O(8)	0.0069(4)	0.1025(3)	0.7184(2)	4.9(1)
H(10)	0.787(1)	0.339(1)	0.710(1)	5.0[b]
H(11)	0.854(1)	0.440(1)	0.776(1)	5.0
H(60)	0.295(1)	0.512(1)	0.947(1)	5.0
H(61)	0.368(1)	0.427(1)	1.031(1)	5.0
H(12)	0.570(1)	0.580(1)	0.548(1)	5.0
H(13)	0.490(1)	0.704(1)	0.426(1)	5.0
H(15)	0.823(1)	0.675(1)	0.339(1)	5.0
H(16)	0.905(1)	0.553(1)	0.462(1)	5.0
H(22)	0.099(1)	0.238(1)	0.825(1)	5.0
H(24)	-0.241(1)	0.117(1)	0.856(1)	5.0
H(26)	-0.062(1)	0.358(1)	1.033(1)	5.0
H(180)	0.480(4)	0.883(3)	0.249(3)	5.5
H(181)	0.481(4)	0.858(3)	0.362(3)	5.5
H(182)	0.420(4)	0.773(3)	0.279(3)	5.5
H(190)	0.765(4)	0.836(3)	0.286(3)	5.5
H(191)	0.704(4)	0.769(3)	0.210(3)	5.5
H(192)	0.635(4)	0.882(3)	0.221(3)	5.5

[a]Equivalent isotropic thermal parameter
[b]Fixed isotropic value

Table 2. Anisotropic Thermal Parameters for $C_{22}H_{17}N_3O_8$[a].

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	.0113(3)	.0065(3)	.0061(3)	.0020(1)	.0035(1)	.0024(1)
C(2)	.0103(3)	.0049(3)	.0050(3)	.0000(1)	.0021(1)	.0076(1)
C(3)	.0105(3)	.0042(3)	.0049(3)	−.0006(1)	.0018(1)	.0004(1)
C(4)	.0094(3)	.0043(3)	.0057(3)	−.0018(1)	.0017(1)	−.0007(1)
C(5)	.0081(3)	.0050(3)	.0058(3)	−.0014(1)	.0010(1)	.0006(1)
C(6)	.0080(3)	.0060(3)	.0054(3)	−.0017(1)	.0010(1)	.0001(1)
C(11)	.0072(3)	.0047(3)	.0049(3)	−.0010(1)	.0025(1)	−.0009(1)
C(12)	.0082(3)	.0055(3)	.0040(3)	−.0004(1)	.0028(1)	−.0006(1)
C(13)	.0079(3)	.0057(3)	.0045(3)	.0003(1)	.0023(1)	.0006(1)
C(14)	.0089(3)	.0054(3)	.0042(3)	−.0016(1)	.0022(1)	−.0001(1)
C(15)	.0097(3)	.0070(3)	.0056(3)	−.0019(1)	.0043(1)	−.0008(1)
C(16)	.0063(3)	.0065(3)	.0051(3)	−.0001(1)	.0027(1)	−.0003(1)
C(17)	.0082(3)	.0053(3)	.0048(3)	.0006(1)	.0028(1)	−.0007(1)
C(18)	.0139(3)	.0046(3)	.0086(3)	−.0007(1)	.0020(1)	.0005(1)
C(19)	.0205(3)	.0071(3)	.0073(3)	−.0035(1)	.0063(1)	.0004(1)
C(21)	.0064(3)	.0047(3)	.0042(3)	−.0002(1)	.0011(1)	.0001(1)
C(22)	.0063(3)	.0052(3)	.0047(3)	.0003(1)	.0018(1)	.0011(1)
C(23)	.0079(3)	.0048(3)	.0035(3)	−.0001(1)	.0009(1)	.0000(1)
C(24)	.0059(3)	.0057(3)	.0057(3)	.0001(1)	.0014(1)	.0013(1)
C(25)	.0066(3)	.0055(3)	.0056(3)	.0004(1)	.0032(1)	.0008(1)
C(26)	.0093(3)	.0050(3)	.0059(3)	.0005(1)	.0032(1)	.0004(1)
C(27)	.0078(3)	.0058(3)	.0052(3)	.0000(1)	.0023(1)	.0011(1)
N(1)	.0131(3)	.0070(3)	.0055(3)	−.0014(1)	.0030(1)	.0018(1)
N(2)	.0101(3)	.0067(3)	.0069(3)	.0014(1)	.0043(1)	.0013(1)
N(3)	.0107(3)	.0069(3)	.0048(3)	−.0003(1)	.0013(1)	.0000(1)
O(1)	.0093(2)	.0062(2)	.0054(2)	.0013(1)	.0037(1)	.0009(1)
O(2)	.0087(2)	.0083(2)	.0073(2)	.0026(1)	.0034(1)	.0004(1)
O(3)	.0076(2)	.0050(2)	.0051(2)	−.0016(1)	.0017(1)	−.0003(1)
O(4)	.0130(2)	.0090(2)	.0082(2)	−.0035(1)	.0052(1)	−.0042(1)
O(5)	.0156(3)	.0090(3)	.0097(3)	−.0007(1)	.0085(1)	−.0011(1)
O(6)	.0097(3)	.0097(3)	.0097(3)	−.0023(1)	.0049(1)	−.0001(1)
O(7)	.0145(3)	.0094(3)	.0082(3)	−.0055(1)	.0033(1)	−.0028(1)
O(8)	.0144(3)	.0098(3)	.0076(3)	−.0016(1)	.0058(1)	−.0020(1)

[a]The tensor is of the form $\exp(-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$

Table 3. Interatomic distances (Å) and angles (°) for $C_{22}H_{17}N_3O_8$.

C(1)-C(2)	1.460(6)	C(24)-C(25)	1.393(6)
C(1)-O(1)	1.448(5)	C(25)-C(26)	1.363(6)
C(2)-C(3)	1.192(6)	C(25)-N(2)	1.480(5)
C(3)-C(4)	1.377(6)	C(27)-O(4)	1.206(5)
C(4)-C(5)	1.173(6)	C(27)-O(3)	1.339(5)
C(5)-C(6)	1.478(6)	N(2)-O(5)	1.244(5)
C(6)-O(3)	1.462(5)	N(2)-O(6)	1.212(5)
C(11)-C(12)	1.403(6)	N(3)-O(7)	1.227(5)
C(11)-C(16)	1.413(6)	N(3)-O(8)	1.228(5)
C(11)-C(17)	1.462(6)		
C(12)-C913)	1.357(6)	C(1)-H(10)	1.06(1)
C(13)-C(14)	1.422(6)	C(1)-H(11)	1.06(1)
C(14)-N(1)	1.354(5)	C(6)-H(60)	1.05(1)
C(14)-C(15)	1.414(6)	C(6)-H(61)	1.07(1)
C(15)-C(16)	1.377(6)	C(12)-H(12)	1.06(1)
C(17)-O(2)	1.198(5)	C(13)-H(13)	1.07(1)
C(17.)-O(1)	1.355(5)	C(15)-H(15)	1.07(1)
C(18)-N(1)	1.449(7)	C(16)-H(16)	1.07(1)
C(19)-N(1)	1.461(7)	C(18)-H(180)	1.06(4)
C(21)-C(22)	1.387(6)	C(18)-H(181)	1.09(4)
C(21)-C(26)	1.391(6)	C(18)-H(182)	0.99(4)
C(21)-C(27)	1.494(6)	C(19)-H(190)	0.98(4)
C(22)-C(23)	1.388(6)	C(19)-H(191)	0.86(4)
C(23)-C(24)	1.379(6)	C(19)-H(192)	1.12(4)
C(23)-N(3)	1.474(5)	C(22)-H(22)	1.07(1)
C(24)-C(25)	1.393(6)	C(24)-H(24)	1.06(1)

C(2)-C(1)-O(1)	106.6(4)	C(22)-C(23)-C(24)	122.7(4)
C(1)-C(2)-C(3)	178.3(5)	C(22)-C(23)-N(3)	119.3(4)
C(2)-C(3)-C(4)	178.4(6)	C(24)-C(23)-N(3)	117.9(4)
C(3)-C(4)-C(5)	177.0(6)	C(23)-C(24)-C(25)	116.1(4)
C(4)-C(5)-C(6)	173.5(5)	C(24)-C(25)-C(26)	123.6(4)
C(5)-C(6)-O(3)	108.3(4)	C(24)-C(25)-N(2)	116.6(4)
C(12)-C(11)-C(16)	117.8(4)	C(26)-C(25)-N(2)	119.7(4)
C(12)-C(11)-C(17)	123.0(4)	C(21)-C(26)-C(25)	118.4(4)
C(16)-C(11)-C(17)	119.2(4)	C(21)-C(27)-O(3)	111.4(4)
C(11)-C(12)-C(13)	122.1(4)	C(21)-C(27)-O(4)	124.3(4)
C(12)-C(13)-C(14)	121.4(4)	O(3)-C(27)-O(4)	124.3(5)
C(13)-C(14)-C(15)	116.3(4)	C(14)-N(1)-C(18)	121.4(4)
C(13)-C(14)-N(1)	121.4(5)	C(14)-N(1)-C(19)	121.1(5)
C(15)-C(14)-N(1)	122.3(5)	C(18)-N(1)-C(19)	117.5(5)
C(14)-C(15)-C(16)	122.4(4)	C(25)-N(2)-O(5)	116.5(4)
C(11)-C(16)-C(15)	120.1(4)	C(25)-N(2)-O(6)	118.7(4)
C(11)-C(17)-O(1)	110.7(4)	O(5)-N(2)-O(6)	124.8(4)
C(11)-C(17)-O(2)	126.6(4)	C(23)-N(3)-O(7)	118.0(4)
O(1)-C(17)-O(2)	122.6(4)	C(23)-N(3)-O(8)	118.3(4)
C(22)-C(21)-C(26)	120.5(4)	O(7)-N(3)-O(8)	123.7(4)
C(22)-C(21)-C(27)	122.3(4)	C(1)-O(1)-C(17)	115.8(4)
C(26)-C(21)-C(27)	117.2(4)	C(6)-O(3)-C(27)	112.4(4)
C(21)-C(22)-C(23)	118.6(4)		

Table 4. Critical parameters for solid-state polimerization of diacetylenes $R-C-C \equiv C-C \equiv C-R$

R	d_1 (Å)	$\gamma_1(^0)$	Polymerization
$-CH_2OH$	5.34	41.4	very readily
$-CH_3$	5.65	42.0	readily
$-CH_2O-\underset{O}{C}-C_6H_5$	4.35	58.8	with difficulty
	6.04	50.9	no polymerization
present compound (asymmetric)	5.56 / 7.31	42.8 / 78.7	no polymerization

POLYMER

MONOMER

FIG. 1

CHAIN AT Y = 0.41

CHAIN AT Y = 0.91

CHAIN AT Y = 0.09

CHAIN AT Y = 0.59

FIG. 2

FIG 3